PATENT SPECIFICATION

COMPLETE SPECIFICATION

Cast Iron

We, INTERNATIONAL NICKEL LIMITED,
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a British Company, of Thames House, Mill-
bank, London, S.W.1, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particularly
described in and by the following state-
ment: —

This invention relates to graphitic cast iron
having controlled graphite structure and an
improved combination of properties.

Flake graphite cast iron, that is to say,
graphitic cast iron in which the graphite is
dispersed in the form of irregularly shaped
flakes, has been used for many years as an
engineering material on an enormous scale.
It has many advantages, notably its cheapness,
its good founding properties, which include
fluidity, resistance to the formation of shrink-
age cavities in castings which are difficult to
feed, freedom from dross effects, and low
chilling tendency, together with generally use-
ful mechanical properties. On the other hand
flake graphite cast iron lacks toughness, owing
to the great number of weakening discontinui-
ties and notches introduced into the structure
of the castings by the graphite flakes.

The most striking advance in the technology
of cast iron in recent years has been the dis-
covery of spheroidal graphite cast iron, in which
some or all of the graphite appears at low
magnifications as compact, soft, grey-coloured,
rounded particles, usually nearly circular in
section, or as conglomerates or groups of
such particles. The occurrence of the graphite
in this form results from the presence in the
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iron as cast of controlled residual amounts of
magnesium, as described and claimed in our
Patent No. 630,070, cerium, as described and 40
claimed in Patent No. 645,862, or both these
elements in combination as described and
claimed in our Patent No. 685,083. The
change in graphite form from flake to spheroi-
dal has made possible the production of cast- 45
ings having very high strength and useful
values of ductility as compared to flake gra-
phite cast iron. Spheroidal graphite cast iron
is now well established as a foundry product,
and its use in the form of castings in industry 50
is expanding each year.

Spheroidal graphite cast iron has, however,
one substantial disadvantage, namely that its
founding properties are not so good as those
of flake graphite cast iron of the same base 55
composition. In particular, it has higher
shrinkage and does not flow so easily, with
the result that it is difficult to produce sound
thin-walled castings of complicated shape in
quantity. An example of such a casting is the 60
cylinder block of an internal combustion
engine for a motor car. Such cylinder blocks
are normally cast in grey iron with flake
graphite, and although the increased strength
of spheroidal graphite cast iron would ob- 65
viously allow a cylinder block to be made
lighter, and so increase the power-to-weight
ratio of the engine, it has not proved prac-
ticable to use spheroidal graphite cast iron for
this purpose. 70

Another disadvantage of spheroidal graphite
cast iron is that its thermal conductivity and
resistance to thermal shock are lower than
those of flake graphite cast iron, and accord-

ingly it has not been much used for the production of such articles as light-weight brake drums and ingot moulds.

Another property in which spheroidal graphite cast iron is deficient in comparison with flake graphite cast iron is its damping capacity, that is its ability to damp vibrations.

Our object in this invention is to produce consistently on an industrial scale cast iron having substantially better founding properties than those of spheroidal graphite cast iron, and mechanical properties substantially greater than those of flake graphite cast iron.

It is known that the introduction of magnesium into cast iron does not always lead to fully spheroidal graphite structures, and indeed it was proposed in our Specification No. 671,467 to produce cast iron with graphite in a form intermediate between flake and spheroidal by using smaller residual magnesium contents than are required to give a fully spheroidal structure. In practice, however, it is impossible by this means to obtain castings with reproducible properties on an industrial scale. The various types of graphite that have been observed have been discussed by Donoho in a paper published in "Modern Castings" for July 1961 at pages 65 to 71, inclusive. The types of graphite described and illustrated by Donoho include one identified as "vermicular" graphite, which has been found from time to time on an unpredictable basis in certain castings. The term "vermicular" graphite is used in this specification and claims in the same sense as by Donoho in the paper referred to above.

The present invention is based on the discovery that a controlled vermicular graphite structure can be produced in graphitic cast iron by incorporating controlled amounts of magnesium and cerium (or other metal of Group IIIB of the periodic table), together with titanium in amounts substantially greater than occur adventitiously in cast iron. The resulting vermicular graphite cast iron is characterised by mechanical properties much better than those of flake graphite cast iron of essentially the same base composition and by founding properties, thermal conductivity, thermal shock resistance and damping capacity better than those of spheroidal graphite cast iron. A typical microstructure of a vermicular graphite iron according to the invention is shown in the accompanying drawing, which is a photomicrograph taken at a magnification of 100 diameters. It will be observed that most of the graphite particles are vermicular in form, the remainder being spheroidal.

In accordance with the invention the graphite in graphitic cast iron is caused to separate predominantly in the vermicular form, i.e. with more than half of the graphite particles in the vermicular form, by incorporating in the iron from 0.005 to 0.06% magnesium, from 0.15 to 0.5% titanium and from 0.001

to 0.015% metal from Group IIIB of the periodic table. Of the Group IIIB metals we prefer to employ cerium or the cerium alloy known as mischmetal, and for convenience this group of metals will be referred to hereinafter as cerium.

It is well known that both magnesium and cerium readily combine with sulphur to form sulphides, and the resultant sulphides may float in the molten iron and be entrapped in the castings. These sulphides do not exert the beneficial effect of elementary magnesium and cerium, and all references to the contents of magnesium and cerium or other Group IIIB metal in the present specification relate to the metals in the elementary form.

The three elements magnesium, titanium and cerium cooperate to control the occurrence of the graphite predominantly in the vermicular form, and it is important that each of them is present within the ranges set forth. If only two of them are present, the desired graphite structure cannot be obtained reliably, if at all, and the properties of the resulting castings are inferior in respect either of strength or founding properties. Substantially the same is true if two of the three elements are present within the defined ranges, and the third element is present in either a lesser or greater amount than the defined range.

When magnesium is absent, or present in amounts less than 0.005%, the graphite occurs in the flake form, and the strength of the iron is reduced. Increasing the cerium content in such irons causes the flake graphite structure to change abruptly from flake to spheroidal. At magnesium contents of 0.005% and above, preferably at least 0.01%, the desired predominantly vermicular graphite structure is obtained when titanium and cerium are also present within the ranges set forth. Advantageously the magnesium content does not exceed 0.04%, and when more than about 0.06% magnesium is present increasing amounts of spheroidal graphite occur in the structure, with an accompanying undesirable increase in chilling tendency and in shrinkage on solidification together with an increased tendency to form dross inclusions which cause surface defects.

When titanium is absent or is present in amounts less than 0.15%, the graphite cannot reliably be obtained in the vermicular form, since the graphite occurs as flake at low magnesium and cerium contents, and the graphite form tends to transform abruptly from flake to spheroidal as the content of either magnesium or cerium is increased above a critical value. Preferably the titanium content is at least 0.2%. On the other hand when the titanium exceeds 0.5% oxide films form on the surface of the liquid iron and tend to cause surface defects on castings poured from it.

When cerium is absent, flake graphite or mixtures of flake and spheroidal graphite are

formed and the strength of the iron is low. On the other hand, when the cerium content exceeds 0.015%, excessive amounts of spheroidal graphite are again formed in the structure and the shrinkage of the resulting castings is undesirably increased. The tendency of such irons to chill is markedly increased even in moderately thick castings. Preferably the cerium content does not exceed 0.01%.

Most advantageously the cast iron of the invention contains from 0.01 to 0.04% magnesium, from 0.2 to 0.5% titanium and from 0.001 to 0.01% of cerium or other metal of Group IIIB of the periodic table.

The chilling tendency, i.e. the tendency for the iron to form massive carbides and so to be white, of the cast iron of the invention is lower than that of a spheroidal graphite cast iron, and in the absence of other carbide-forming elements it is approximately proportional to the magnesium content. For castings in which a low chilling tendency is required, for example those having section sizes of one-quarter inch or less, it is therefore desirable to use magnesium contents at the lower end of the ranges set forth, e.g. about 0.01%.

The cast iron of the invention may be either alloyed or unalloyed, and it may have any matrix structure characteristic of alloyed and unalloyed graphite cast iron in the as-cast or heat-treated conditions. For example the as-cast matrix microstructure may be ferritic, pearlitic, austenitic, martensitic or acicular. Generally speaking the base composition of the iron may contain from 2 to 4% carbon, from 1.5 to 3.5% silicon, from 0.1 to 2.5% manganese, up to 0.2% phosphorus, and not more than 0.025% sulphur. Preferably the carbon content is from 3 to 3.6%, the silicon content is from 2 to 2.6%, the manganese content is from 0.2 to 0.7% and the sulphur content is not more than 0.02%.

Nickel is an important alloying element, and may be present in amounts up to 36%. The addition of nickel improves the properties of the matrix, particularly its strength, and does not detrimentally affect the graphite structure. Thus, at nickel contents up to about 5%, each additional per cent of nickel may increase the tensile strength of the castings by about 6,000 pounds per square inch (p.s.i.). At nickel contents above about 20%, the matrix becomes austenitic.

The carbide-forming elements chromium, molybdenum and vanadium do not appear to affect the formation of the desired vermicular graphite structure, and the iron may contain up to 1% chromium, up to 2% molybdenum and up to 0.5% vanadium. These elements do however increase the chilling tendency of castings containing them, and they are therefore to be avoided when it is important to prevent the chill of the castings. However, in the presence of nickel in amounts sufficient to render the matrix austenitic, the contents both of the carbide-forming elements chromium, molybdenum and vanadium, and of manganese, may be higher than those set forth above. For example, austenitic castings may contain about 2% of chromium.

Zirconium is an element which may advantageously be present in that it appears to have the same effect as titanium, but the loss of zirconium when this is added to molten iron is such that it is difficult to produce an iron with a residual zirconium content of more than 0.05%.

The elements copper, tin, lead, antimony and bismuth are undesirable impurities, since they interfere with the controlled production of vermicular graphite. In fact, in the presence of the substantial amounts of titanium which are included in the irons according to the invention these elements have the surprising effect of tending to form spheroidal graphite. Thus, when the magnesium content is 0.04%, or above the copper content should not exceed 0.5% and the tin content should not exceed 0.03%. As the magnesium content is decreased below 0.04%, the tolerances for copper and tin are increased until at a magnesium content of about 0.02%, a copper content up to 2% and a tin content up to 0.15% may be permitted without an undesirable formation of spheroidal graphite being encountered. The lead content should not exceed 0.01%, and the antimony and bismuth contents should not exceed 0.01% each.

Aluminium is a particularly undesirable element and is not employed as a deliberate addition. This element is detrimental to founding properties, since it produces a sticky, slaggy melt of decreased fluidity and yields a drossy casting having a poor surface, particularly on the cope side. The aluminium content should therefore not exceed 0.05%. Boron is another undesirable element, since it strongly tends to form massive cementites and other undesirable forms of carbide which are difficult to remove by annealing the castings. Accordingly the content of this element should not exceed 0.002%.

The cast iron of the invention may be produced with the use of any type of furnace commonly employed in the production of foundry grey cast iron. It is important that the melt to be treated should have such graphitising power that if cast, if necessary after graphitising inoculation, it would be a grey cast iron substantially devoid of massive carbides such as occur in white cast iron. If the sulphur content of the melt exceeds 0.02%, it is advantageous to lower it to 0.02%, or less by means of common desulphurising techniques before incorporating the controlled amounts of magnesium and cerium. This is particularly important if the residual content of magnesium should be

low, e.g. 0.01%. Desulphurisation may if
desired be effected by a preliminary treatment
with magnesium.
    After bringing the melt to a suitable casting
temperature, e.g. in the range 1425 to 1540°
C, additions of cerium or other Group IIIB
element, magnesium and titanium are made
to provide residual contents of these elements
within the ranges set forth above. Titanium
is commonly found in cast iron in small
amounts less than those required by the in-
vention, whereas magnesium, cerium and other
Group IIIB elements are not usually present.
The amount of titanium contained in the
molten cast iron should therefore be ascer-
tained and only the amount of titanium re-
quired to adjust the titanium content of the
bath to the required final level should be
incorporated in the bath.
    Shortly before casting, an addition of gra-
phitising inoculant is made to the treated melt,
suitably in an amount sufficient to introduce
at least 0.3% silicon, e.g. 0.3 to 0.7% silicon,
and the melt is then cast. A suitable inoculant
is a ferrosilicon alloy containing 85% silicon,
0.5% calcium and the balance iron. When
castings of thin section, e.g. one eighth inch
or less, are to be made, the "instant inocula-
tion" procedure may advantageously be em-
ployed, wherein a few grams of powdered
inoculating alloy, e.g. ferrosilicon, is intro-
duced into the feeder gate of the mould prior
to pouring the casting. Castings produced in
accordance with the invention may if desired
be heat-treated in known manner to decom-
pose carbides or pearlite.
    As mentioned above, elements from Group
IIIB of the periodic table other than cerium,

for example yttrium, lanthanum or other ele-
ment of the lanthanide or rare earth metal
series may be employed in the place of cerium.
References to the "periodic table" herein are
made to the "Periodic Chart of the Ele-
ments" set forth at pages 56 and 57 of
"Handbook of Chemistry", compiled and
edited by Norbert Adolf Lange, Tenth Edi-
tion, McGraw-Hill Book Company, 1961.
Mischmetal, which generally contains about
50% cerium and about 25% lanthanum, the
balance being other rare earth elements, is a
satisfactory cerium-containing addition mat-
erial for the production of castings in accord-
ance with the invention. It is found in prac-
tice that when such a mischmetal alloy is
added to molten cast iron lanthanum recovery
is only about one-half as great as is the cerium
recovery. It will be appreciated that cerium
or other Group IIIB metal can be added to
the molten cast iron either in the metallic
form or in the form of a compound, e.g. an
oxide, which is reducible to metal in the
bath.
    By way of example, the compositions of 22
castings of irons in accordance with the in-
vention are set out in Table I and their tensile
properties and hardness, determined from 1
inch keel bar castings in the as-cast condition,
are set out in Table II. The last column in
Table II indicates the graphite structure ob-
served in castings of iron of 2 inch section.
Each of the castings in Table I was produced
using a mischmetal alloy containing about
50% cerium and about 25% lanthanum and
contained cerium and lanthanum in a ratio of
about 4 to 1. The balance of each composition
was iron.

TABLE I

Iron No.	Composition (% by weight)							
	C	Si	Mn	Mg	Thi	Ce+La	S	Other
1	3.34	2.53	0.23	0.013	0.15	0.004	0.015	—
2	3.44	2.59	0.24	0.023	0.23	0.006	0.015	—
3	3.23	2.56	0.25	0.007	0.28	0.009	0.025	<0.002Pb
4	3.40	2.57	0.25	0.016	0.27	0.006	0.015	<0.002Pb
5	3.43	2.61	0.25	0.023	0.27	0.005	0.015	<0.002Pb
6	3.31	2.57	0.24	0.013	0.28	0.006	0.015	0.005Pb
7	3.36	2.54	0.25	0.011	0.29	0.005	0.016	0.005Pb
8	3.43	2.54	0.25	0.019	0.28	0.007	0.015	0.005Pb
9	3.61	2.20	0.14	0.042	0.20	0.007	0.020	—
10	3.68	2.10	0.13	0.015	0.22	0.005	0.015	—
11	3.27	2.26	0.31	0.013	0.31	0.005	0.015	—
12	3.33	2.33	0.29	0.014	0.27	0.005	0.017	0.78 Ni
13	3.20	2.41	0.29	0.019	0.24	0.005	0.015	1.58 Ni
14	3.28	2.28	0.43	0.015	0.34	0.007	0.019	—
15	3.27	2.40	0.63	0.017	0.29	0.0055	0.015	—
16	3.26	2.31	0.29	0.016	0.30	0.005	0.019	0.12 Cr
17	3.22	2.36	0.29	0.017	0.25	0.006	0.018	0.15 Pb
18	3.5	2.3	0.3	0.023	0.33	0.006	0.015	—
19	3.50	1.73	0.65	0.015	0.35	0.003	0.015	—
20	3.26	1.89	0.33	0.107	0.34	0.003	0.015	—
21	3.07	2.28	0.41	0.013	0.35	0.006	0.015	—
22	3.5	2.3	0.3	0.008	0.23	0.006	0.015	—

TABLE II

Iron No.	Tensile Strength *k.s.i.	Yield Strength k.s.i.	Elongation, %	Modulus p.s.i.	Hardness BHN	Vermicular Graphite Structure (Bal. Spheroidal)
1	47.4	38.1	5.5	20.7×10^6	137	80%
2	49.4	39.9	6.5	20.9×10^6	140	60%
3	46.2	38.3	4	20.0×10^6	143	90%
4	50.1	40.8	5.5	20.0×10^6	148	80%
5	51.2	41.3	7.5	20.7×10^6	140	70%
6	42.8	34.8	4.5	19.1×10^6	131	90%
7	45.4	36.5	5.5	23.0×10^6	131	70%
8	48.9	39.5	5.5	17.8×10^6	137	60%
9	47.3	38.8	6	21.0×10^6	136	90%
10	44.6	36.0	6	20.7×10^6	—	90%
11	49.1	40.4	2.3	22.6×10^6	156	95%
12	53.6	45.6	1.8	22.5×10^6	163	90%
13	58.7	50.7	1.5	21.6×10^6	187	90%
14	54.3	43.9	1.8	20.0×10^6	174	90%
15	55.2	46.0	2.0	22.5×10^6	179	95%
16	51.1	43.7	1.8	21.6×10^6	179	90%
17	52.1	44.2	2.0	22.7×10^6	168	95%
18	52.5	43.9	6.5	—	143	70%
19	53.8	41.7	2.5	—	178	98%
20	51.1	40.7	2.0	—	163	95%
21	47.4	44.0	1.0	—	170	100%
22	53.7	43.9	7.5	—	140	80%

*k.s.i. = thousands of pounds per square inch.

Castings of two further irons, Nos. 23 and 24, were prepared in the same way in a range of section sizes. The compositions of the irons are set out in Table III are their properties and microstructure in Table IV. The results in Table V show that the vermicular graphite structure of the irons is not greatly affected by variations in section size over the range one-quarter inch to 2 inches. It will also be observed that the tensile properties are not affected by variations in section size to any greater extent than are the properties of ordinary flake graphite cast irons.

TABLE III

Iron No.	Composition (% by weight)							
	C	Si	Mn	Mg	Ti	Ce	Ni	Fe
23	3.53	1.86	0.47	0.018	0.31	0.005	—	bal
24	3.48	1.90	0.40	0.023	0.28	0.005	1.53	bal

TABLE IV

Iron No.	Section Size inches	Tensile Strength, k.s.i.	Yield Strength, k.s.i.	Elongation, %	BHN	% Vermicular graphite (Bal. spheroidal)
23	1/4	68.0	48.3	3.0	194	90
	1/2	60.5	43.4	4.0	187	75
	1	54.5	40.4	3.0	168	95
	2	49.2	37.3	3.0	149	90
24	1/4	86.1	63.0	3.0	222	90
	1/2	73.2	53.2	5.0	207	60
	1	61.9	47.6	2.5	196	70
	2	58.3	44.9	3.0	179	80

The thermal conductivity and damping capacity of a typical iron according to the invention were also determined and compared with those of flake graphite and spheroidal graphite irons of the same base composition, with the results set out in Table V. Damping capacities were determined by applying to specimens of the test materials a vibrational stress initially varying between 4000 p.s.i. in compression and 1000 p.s.i. in compression and measuring the relative rates at which the amplitude of vibration decreased initially when the imposed vibration was shut off.

TABLE V

Material	Thermal conductivity Cal./cm².sec./cm./°C	Relative Damping Capacity
Vermicular graphite iron of this invention	about 0.11	0.6
Flake graphite iron	about 0.12	1.0
Spheroidal graphite iron	about 0.08	0.34

In order to demonstrate the improved feeding properties of the vermicular graphite cast iron of the invention as compared with spheroidal graphite cast iron, valve body test castings of complicated configuration were made in identical moulds designed to provide poor feeding conditions. The cast iron of the invention contained 3.73% carbon, 2.21% silicon, 0.18% manganese, 0.010% magnesium, 0.25% titanium, 0.009% cerium and had graphite in the vermicular form. The spheroidal graphite iron casting was made in the same base iron and contained about 0.05% magnesium. The castings were sectioned longitudinally, and it was found that the casting according to the invention was almost completely sound while the spheroidal graphite iron casting was characterised by severe shrinkage cavities in the poorly fed areas.

The vermicular graphite cast iron of the invention is particularly suitable for use in making cast cylinder blocks for internal combustion engines, ingot moulds and brake drums, particularly brake drums cast integrally with the hub. It may also be employed for a wide range of other castings requiring its advantageous combination of properties, including pumps, valves, cam shafts, gears, gear boxes, and gear carriers, internal combustion engine cylinder heads, piston rings, sealing rings, heat-treating pots, paper mill rolls, machine beds and frames, transmission cases and the like.

WHAT WE CLAIM IS:—

1. Alloyed or unalloyed graphitic cast iron containing from 0.005 to 0.06% magnesium, from 0.15 to 0.5% titanium and from 0.001 to 0.015% metal from Group IIIB of the periodic table and as cast having a microstructure in which the graphite is present predominantly in the vermicular form.

2. Cast iron according to claim 1 in which the magnesium content is from 0.01 to 0.04%, the titanium content is from 0.2 to 0.5% and the content of Group IIIB metal is from 0.001 to 0.01%.

3. Cast iron according to claim 1 or claim 2 having a carbon content from 2 to 4%, a silicon content from 1.5 to 3.5%, a manganese content from 0.1 to 2.5%, a phosphorus content not more than 0.2% and a sulphur content not more than 0.025%.

4. Cast iron according to claim 3 in which the carbon content is from 3 to 3.6%, the silicon content is from 2 to 2.6%, the manganese content is from 0.2 to 0.7% and the sulphur content is not more than 0.02%.

5. Cast iron according to any one of claims 1 to 4 in which the Group IIIB metal is wholly or predominantly cerium.

6. An engine cylinder block cast in iron in accordance with any one of claims 1 to 5.

7. An ingot mould cast in iron in accordance with any one of claims 1 to 5.

8. A brake drum cast in iron in accordance with any one of claims 1 to 5.

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